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(54) **Image receiving paper for colour inkjet printing with aqueous inks**

Aufzeichnungsmaterial für mehrfarbiges Tintenstrahldruckverfahren mit wässrigen Tinten

Feuille réceptrice pour l'impression en couleurs par jet d'encre utilisant des encres aqueuses

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EP-A- 0 718 113 **WO-A-97/01447**

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EP 0 893 271 B1

Description

[0001] The invention relates to image receiving paper suitable more particularly for printing with aqueous inks in a colour inkjet printing technique. The image receiving paper according to the invention comprises a paper support, a water repellent-layer on at least one side and above it an ink receiving layer or set of ink receiving layers.

[0002] Inkjet printing techniques, particularly those using mainly aqueous inks, have undergone rapid development in recent years, both in respect of reliability and the image quality that the printing apparatus can achieve, and in respect of the cost price of the printing apparatus. As a result, the range of application of inkjet printing has been increasingly extended and this technique is now also used for making colour prints required to satisfy relatively high quality requirements, e.g. the printing of colour posters and display graphics in the graphic arts. Quality improvement of inkjet devices of course leads to a continuing demand for improved inks, for example inks having greater colour-fastness, and improved image receiving materials.

[0003] Image receiving materials for multi-colour inkjet printing are usually provided with an ink receiving layer or set of such receiving layers, in which one or more water-accepting binders are present. In order to bind the dyes from the inks, the image receiving layer may contain additives such as filler or fillers and/or a cationic compound. Typical cationic compounds are quaternary ammonium compounds and polymers or copolymers which bear quaternary ammonium groups. The composition of the ink receiving layer is preferably such that the ink droplets sprayed on to the ink receiving layer during the image forming process are rapidly absorbed in the ink receiving layer without flowing out laterally excessively, so that sharp image edges and clean colour tints can be obtained. The dye from the inks must also be fixed preferably rapidly in a thin layer portion of the ink receiving layer, in order to provide images of adequate contrast and adequate high optical density.

[0004] The amount of water and organic solvent locally applied to the image receiving material in printing a multi-colour image with aqueous inks may be very high and may even be more than 30 g of liquid (mostly water) per m² where very dark tints are to be reproduced. When paper receiving materials are used, the problem arises that the liquid penetrates into the paper support via the ink receiving layer, and here it is absorbed by the paper fibres so that the latter swell and the paper bulges locally. The bulges continue even after the print is dry, because the paper fibres do not shrink to their original dimension. Apart from the fact that the quality impression of the print is less satisfactory due to the bulges in the paper, there is the disadvantage that the prints jam or are difficult to introduce or cannot be introduced into finishing machines, e.g. plasticising machines.

[0005] US Patent No. 4 892 782 proposes to subject

paper to possible extra treatment with a water-repellent substance before applying the ink receiving layer, in order to give the paper fibres greater resistance to water. The ammonium salt of styrene/maleic acid anhydride copolymer is indicated as a water-repellent substance. Sizing the paper with this substance is inadequate if large quantities of ink, as indicated hereinbefore, are applied locally to the ink receiving material. This treatment should be regarded as a moisture control resulting in a more vertical than lateral penetration, rather than a treatment resulting in a distinctly reduced moisture absorption by the paper fibres themselves.

[0006] International Application WO 97/01447 discloses image receiving material for aqueous inkjet printing which comprises a support, a porous, water-absorbing layer comprising latex binder, hydrophilic silica and water-soluble viscosity modifier and over this layer a layer composed of a water-soluble cationic polymer. The two layers together forming the ink absorbing composition.

[0007] The invention relates to improved image receiving paper according to the introduction, which is characterised in that the water-repellent layer contains binder and filler and the paper provided with the water-repellent layer has a maximum Cobb 30 value of 5.

[0008] It has been found that an inkjet receiving paper provided with a water-repellent layer as defined hereinbefore beneath the ink receiving layer is satisfactorily resistant to the action of the liquid, mainly aqueous, ink constituents, so that the paper fibres hardly swell, if at all, even at the places where large quantities of ink of about 35 g/m² are applied to form darker colour tints, and substantially flat prints are obtained which can be processed in a finishing machine, such as a plasticising machine, without feed or transport malfunction repeatedly occurring.

[0009] In addition, the water-repellent layer has a relatively low weight and in principle it can be applied together with the ink receiving layer to the paper support in one machine operation, this being favourable for considerations of cost.

[0010] Since filler is also present in the water-repellent layer, the result is that the layer has a somewhat rough surface and hence a large contact surface so that adequate adhesion is obtained between the substantially hydrophilic upper ink receiving layer and the hydrophobic underlying water-repellent layer.

[0011] As already stated, the paper provided with the water-repellent layer should have a maximum Cobb 30 number of 5, which means that the paper absorbs less than 5 g/m² in a Cobb test with a penetration time of 30 seconds. The Cobb test for measuring liquid absorption in paper and other materials is carried out as described in the ISO 535:1991(E) Standard. Of course the Cobb test is carried out on that side of the paper where the water-repellent layer is situated, on which the ink receiving layer will be subsequently applied.

[0012] The following equipment and aids are used for

performing the Cobb test:

- A hollow metal cylinder having a diameter of 112.80 mm and a height of ± 40 mm, one of the end surfaces being polished smooth.
- A flat metal plate covered on one side with a smooth layer of rubber so that when the cylinder is clamped on the rubber and filled with water no leakage occurs. The rubber layer has dimensions such that after the cylinder has been fitted the rubber projects from the cylinder at least 10 mm everywhere.
- A metal clamp by means of which the cylinder is clamped against the sample for measurement and the rubber beneath it, so that no leakage occurs.
- Blotting card having a weight of about 250 g/m² and an absorption of about 70 mm measured in accordance with NEN 1837 with distilled water.

[0013] The paper samples on which the Cobb test is carried out measure 140 x 140 mm. They are conditioned at 20°C and 50% relative humidity for 24 hours before the measurement. The measurement itself is carried out with distilled water at a temperature of 20°C (± 1 °C). The Cobb test is also carried out as described in ISO 535:1991(E). The value of 5 maximum as defined here for Cobb 30 is the average of 5 measurements.

[0014] The water-repellent layer contains one or more substantially hydrophobic film-forming binders and one or more fillers. Suitable binders for forming the water-repellent layer include polyvinyl chloride, polyacrylates and polymethacrylates, copolymers of vinyl chloride with vinyl acetate and possibly an unsaturated carboxylic acid, copolymers of styrene with butadiene and possibly acrylonitrile, copolymers of styrene with acrylonitrile and copolymers of acrylonitrile with butadiene, copolymers of styrene with an acrylate and/or methacrylate, polyvinylidene chloride and copolymers of polyvinylidene chloride.

[0015] Suitable fillers include clay, kaolin, talcum, silica, calcium carbonate (chalk), diatomaceous earth, barium sulphate, titanium dioxide, aluminium oxide, zinc oxide, synthetic fillers, and mixtures of two or more of the above fillers. The filler in the layer serves to give the same a certain roughness and enlarged contact surface and thus provide adequate adhesion of the hydrophilic ink receiving layer to be applied thereto. The filler content in the water-repellent layer may not be so high that the layer becomes water permeable. Generally, the ratio by weight of filler to polymer binder should be less than 1:1 in order to obtain a Cobb 30 value of 5 maximum.

[0016] The preferred filler to binder ratio in order, on the one hand, to give an adequately low Cobb value (less than 5) in order to protect the paper fibres against the effect of moisture and, on the other hand, obtain sufficient roughness to cause the ink receiving layer to adhere, depends inter alia on the nature of the filler and binder, the particle size and the surface nature of the filler particles, particularly their porosity/specific surface

area.

[0017] When fillers are used such as synthetic amorphous silicas having a particle size of 3 to 4 micrometers and a large pore volume greater than about 0.4 ml/g, the preferred quantity of filler has been found to be generally 0.15 - 0.45 parts by weight per part by weight of binder. When fillers are used with approximately the same particle size but a much less pore volume the preferred quantity of filler is 0.6 - 1 part by weight per part by weight of binder. The water-repellent paper should completely cover the paper support to provide good protection of the paper fibres against the influence of moisture. The dry weight of the layer should not be greater than required to achieve a Cobb 30 value of 5 maximum. Generally, the dry weight of the water-repellent layer should be between 4 and 7 g/m².

[0018] The water-repellent layer can be applied to the paper support by means of a coating liquid based on one or more organic solvents in which film-forming binder is dissolved or dispersed and filler is dispersed. Preferably, they are applied from a substantially aqueous dispersion of binder and filler.

[0019] Very suitable water-repellent layers are the filler-containing layers formed by means of an aqueous dispersion and containing as binder a copolymer of 50 - 75% by weight of styrene and 50 - 25% by weight of butadiene and, as filler, synthetic amorphous silica, and wherein the filler to binder ratio by weight is 0.15 to 0.40. The dry weight of the layer is preferably 4 - 6 g/m². The Cobb 30 value of such a layer is about 3.5.

[0020] The water-repellent layer is applied to both sides of the paper support, or at least to the side where the ink receiving layer is also applied.

[0021] If the water-repellent layer is also applied to the back (i.e. to a side where subsequently no ink receiving layer is applied, it may have the same composition as the other water-repellent layer but a lower dry weight, or another composition resulting in a higher Cobb value, e.g. 7 to 8. The higher Cobb value is permissible because the back of the paper has to process less moisture than the front bearing the ink receiving layer. Substances such as lubricants, which promote paper transport in the printing apparatus, can be added to the back layer.

[0022] The ink receiving layer applied above the water-repellent layer may be one of the layers known for the reception of aqueous inkjet inks, or a set of layers. Such layers or combinations of layers applied above one another are known in many embodiments and generally consist of one or more absorbent fillers, one or more water-soluble or swellable binders, and one or more cationogenic substances, which may or may not be polymeric, and which are adapted to bind the dyes from the aqueous inks. The cationogenic substances best known for this purpose are (polymeric) quaternary ammonium compounds.

[0023] The invention will now be explained with reference to the following examples.

Example 1

[0024] White base paper of a weight of about 80 g/m² (type Xerographic BEX made by Champion, Brazil) was provided on both sides with a water-repellent layer having a dry weight of 6 g/m², by means of a liquid having the following composition:

100 ml	of a dispersion (50 g/litre) of a copolymer of styrene with butadiene in water (Dow Latex 905 made by Dow Chemical, Netherlands)
50 g	of crystalline silica (Min-u-sil 5 micrometer, of Pennsylvania Glass Sand, USA)
100 ml	of water

[0025] The Cobb value measured at the side where the water-repellent layer was applied was 2.3 (average of 5 measurements on 5 different samples).

[0026] The paper provided with a water-repellent in this way was provided on one side with an ink receiving layer of a dry weight of 10 g/m² using a liquid containing:

150 ml	of a 10% by weight solution of polyvinyl alcohol in water (Mowiol 40-80 made by Hoechst AG, Germany)
15 g	of silica (Syloid 72 of W.R. Grace & Co., USA)
5 g	of quaternary ammonium polymer (Alcolstat 167 by Allied Colloids, England)
150 ml	of water

[0027] The inkjet receiving paper obtained in this way was imaged in an inkjet printer, type Encad, Novajet. Pro, with a multi-colour image containing dark colour zones, the ink application locally being more than 30 g/m². No excess swelling of the paper fibres occurred and after drying the print obtained was completely flat (A4 format) and it was possible to process it without difficulty in a plasticising machine.

Example 2

[0028] Inkjet receiving paper was made in a similar manner to that described in Example 1, the liquid used for forming the water-repellent layer with a dry weight of about 5 g/m² being a liquid of the following composition:

100 g	of Dow Latex 905 (see Example 1)
23 g	of amorphous synthetic silica (Tixosil 311 by Rhône Poulenc, France)
100 ml	of water

[0029] The measured layer had a Cobb value of 3.5 (average value of 5 measurements). The quality of the multi-colour prints generated in an inkjet printer (see Example 1) was substantially identical to that of prints obtained with the paper of Example 1.

Example 3

[0030] Inkjet receiving paper was made by the method of Example 1, the water-repellent layer now being formed in a dry weight of about 6 g/m² with the following coating liquid:

100 ml	of a 50% by weight aqueous styrene/acrylate emulsion (Litex AP4120 by Hüls A.G., Germany)
40 g	of calcium carbonate (Microcal spa C100 by ECC International, Belgium)
80 ml	of water

[0031] The Cobb value was 4.3 (average of 5 measurements).

[0032] The prints obtained with this paper in the printer used in accordance with Example 1 were substantially identical to those obtained with papers in accordance with the preceding Examples.

Example 4

[0033] The paper provided with a water-repellent layer in accordance with the method of Example 1 was coated with an ink receiving layer having a dry weight of about 10 g/m² by means of a liquid of the following composition:

50 ml	of a 20% by weight aqueous solution of polyvinyl alcohol (Mowiol 8-88 of Hoechst A.G., Germany)
75 ml	of a 15% by weight aqueous solution of polyvinyl pyrrolidone (PVP K90 of G.A.F. USA)
125 ml	of water

[0034] The multi-colour prints obtained with this paper in an inkjet printer in accordance with Example 1 were of good quality and the paper support exhibited no bulging as a result of water absorption.

[0035] If the ink receiving layer used in the preceding Examples (or another ink receiving layer known per se) is applied to the paper support directly, i.e. without the intermediate water-repellent layer, or is applied to a paper support treated with 6 g/m² dry weight of a styrene/maleic acid anhydride (ammonium salt) as described in US Patent 4 892 782, the prints obtained when printing in the apparatus mentioned in Example 1 are not flat and result in repeated transport malfunctioning in a plasticising machine.

Claims

1. An image receiving paper suitable for printing with aqueous inkjet inks, comprising a paper support provided on at least one side with a water-repellent layer and above it an ink receiving layer or set of ink

receiving layers, **characterised in that** the water-repellent layer contains binder and filler and the paper provided with the water-repellent layer has a maximum Cobb 30 value of 5.

2. An image receiving paper according to claim 1, **characterised in that** the dry weight of the water-repellent layer is 7 g/m² maximum.
3. An image receiving paper according to claim 1, **characterised in that** the filler:binder ratio by weight in the water-repellent layer is ≤ 1 .
4. An image receiving paper according to claim 3, **characterised in that** the filler:binder ratio by weight is between 0.15 and 0.45.
5. An image receiving paper according to any one or more of the preceding claims, **characterised in that** the water-repellent layer contains a binder from the group formed by polyvinyl chloride, polyacrylates, polymethacrylates, copolymer of vinyl chloride with vinyl acetate and possibly unsaturated carboxylic acid, copolymer of styrene with butadiene and possibly acrylonitrile, copolymer of styrene and acrylonitrile, copolymer of butadiene and acrylonitrile.
6. An image receiving paper according to claim 4, **characterised in that** the binder is a copolymer of 50 to 75% by weight styrene and 50 - 25% by weight butadiene.
7. An image receiving paper according to claim 6, **characterised in that** it contains per part by weight of binder between 0.15 and 0.45 parts by weight of filler having a pore volume greater than 0.4 ml/g.
8. An image receiving paper according to claim 7, **characterised in that** the filler is synthetic amorphous silica.

Patentansprüche

1. Bildaufzeichnungspapier für das Drucken mit wässrigen Tintenstrahl-tinten, mit einem Trägerpapier, das auf wenigstens einer Seite mit einer wasserabstoßenden Schicht und darüber mit einer Farbaufnahmeschicht oder einem Satz aus Farbaufnahmeschichten versehen ist, **dadurch gekennzeichnet, daß** die wasserabstoßende Schicht Bindemittel und Füllmaterial enthält und das mit der wasserabstoßenden Schicht versehene Papier einen maximalen Cobb 30 Wert von 5 hat.
2. Bildaufzeichnungspapier nach Anspruch 1, **dadurch gekennzeichnet, daß** das Trockengewicht

der wasserabstoßenden Schicht höchstens 7 g/m² beträgt.

3. Bildaufzeichnungspapier nach Anspruch 1, **dadurch gekennzeichnet, daß** das Gewichtsverhältnis von Füllmaterial: Bindemittel in der wasserabstoßenden Schicht ≤ 1 ist.
4. Bildaufzeichnungspapier nach Anspruch 3, **dadurch gekennzeichnet, daß** das Gewichtsverhältnis von Füllmaterial : Bindemittel zwischen 0,15 und 0,45 beträgt.
5. Bildaufzeichnungspapier nach einem oder mehreren der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** die wasserabstoßende Schicht ein Bindemittel aus der Gruppe enthält, die gebildet wird durch Polyvinylchlorid, Polyacrylate, Polymethacrylate, Copolymere von Vinylchlorid mit Vinylacetat und ggf. ungesättigter Carbonsäure, Copolymer von Styrol mit Butadien und ggf. Acrylonitril, Copolymer von Styrol mit Acrylnolotril, Copolymer von Butadien und Acrylnolotril.
6. Bildaufzeichnungspapier nach Anspruch 4, **dadurch gekennzeichnet, daß** das Bindemittel ein Copolymer aus 50 bis 75 Gew.% Styrol und 50 - 25 Gew.% Butadien ist.
7. Bildaufzeichnungspapier nach Anspruch 6, **dadurch gekennzeichnet, daß** es je Gewichtsteil Bindemittel zwischen 0,15 und 0,45 Gewichtsteile Füllmaterial mit einem Porenvolumen von mehr als 0,4 ml/g enthält.
8. Bildaufzeichnungspapier nach Anspruch 7, **dadurch gekennzeichnet, daß** das Füllmaterial synthetisches amorphes Silika ist.

Revendications

1. Papier pour la réception d'images approprié pour l'impression avec des encres aqueuses pour jet d'encre, comprenant un support en papier muni sur au moins une face d'une couche repoussant l'eau et, sur cette couche, d'une couche de réception d'encre ou d'un jeu de couches de réception d'encre, **caractérisé en ce que** la couche repoussant l'eau contient un liant et une charge et **en ce que** le papier muni de la couche repoussant l'eau à un indice Cobb 30 de 5 au maximum.
2. Papier pour la réception d'images selon la revendication 1, **caractérisé en ce que** le poids sec de la couche repoussant l'eau est de 7 g/m² au maximum.

3. Papier pour la réception d'images selon la revendication 1, **caractérisé en ce que** le rapport en poids charge : liant dans la couche repoussant l'eau est ≤ 1 .
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4. Papier pour la réception d'images selon la revendication 3, **caractérisé en ce que** le rapport en poids charge : liant est compris entre 0,15 et 0,45.
5. Papier pour la réception d'images selon une ou plusieurs des revendications précédentes, **caractérisé en ce que** la couche repoussant l'eau contient un liant pris dans le groupe formé par chlorure de polyvinyle, polyacrylates, polyméthacrylates, copolymères de chlorure de vinyle et d'acétate de vinyle et éventuellement d'un acide carboxylique insaturé, copolymère de styrène et de butadiène et éventuellement d'acrylonitrile, copolymère de styrène et d'acrylonitrile, copolymère de butadiène et d'acrylonitrile.
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6. Papier pour la réception d'images selon la revendication 4, **caractérisé en ce que** le liant est un copolymère de 50 à 75% en poids de styrène et de 50-25% en poids de butadiène.
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7. Papier pour la réception d'images selon la revendication 6, **caractérisé en ce qu'il** contient par partie en poids de liant entre 0,15 et 0,45 partie en poids de charge ayant un volume de pores de plus de 0,4 ml/g.
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8. Papier pour la réception d'images selon la revendication 7, **caractérisé en ce que** la charge est de la silice amorphe synthétique.
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